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Recycled wastes as precursor for synthesizing wollastonite

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Abstract

The application of wollastonite in various industries has attracted the attention of scientists to synthetically produce it. Also, the ecological demands of a healthy and safe environment urged them to utilize the industrial wastes accumulating year after year and threatening the environment.

Therefore, three groups of experiments were designed to prepare wollastonite based on the application of natural stone processing wastes and silica fumes as well as pure chemicals. The high degree of fineness of the waste precursors and the presence of impurities in the form of alkali and iron oxides enhanced the formation of wollastonite at 1100 °C. While, the pure precursors failed to give wollastonite even after firing at 1400°C.

Different ratios of $CaO:SiO_2$ comprising 1:1, 1:1.125, 1:1.166 and 1:1.25 were studied. XRD results revealed that the ratio 1:1.125 gives wollastonite as a sole phase. Lower and higher ratios cause the formation of other calcium silicate phases or free cristobalite.

Keywords: A. Powders: solid state reaction; D. Silicate

1. Introduction

Recycling of industrial wastes and byproducts is becoming a crucial demand by the ecological legislation to achieve a healthy environment without any threat to the living organisms; human, animals and plants.

The growth in the world population, lead to an expansion in housing and to the growth in certain industries as building and construction industries. Moreover, the rise in the standard of living caused a remarkable growth in the ceramic tile and natural ornamental stones processing industries. As a result, huge proportion of wastes of very fine nature, product of the rock processing accumulates, and how to get rid of it became a serious problem.

The development in the firing technique of ceramic tiles urged to find a proper way for the application of limestone or other carbonates as dolomite in their recipes. This problem was solved through the processing of these rocks and adding them as synthetic minerals [1–3]. Production of wollastonite became a solution for getting over the accumulation of the wastes and forming a suitable precursor for the tile industries. A specific feature of natural wollastonite is the fact that it reduces dimensional changes during drying and firing of ceramic products.

Wollastonite has found its application in the production of heat-insulating ceramics, foundry lining, and packing in the metallurgy and automobile industry as well as a filler in paints and polymers. The world demand for wollastonite is currently expanding in particular to replace asbestos which is health hazardous, in the different industries. In the ceramic industry it is introduced into the composition of special electrotechnical porcelain, which has low dielectric losses, and into sanitary porcelain and earthenware. A new field of application of wollastonite is in the bioactive ceramic material; as bioglass [4] for bone substitution and as coating [5].

Wollastonite occurs in three polymorphic forms; low temperature triclinic form [1T], monoclinic form or the so-called *para*-wollastonite [2M] and the high temperature form pseudo-wollastonite which occurs in the pseudo-hexagonal form [6]. The conversion of the low temperature form to the high temperature form takes place at 1125 °C [7].

The fever for the industrial production of synthetic wollastonite dates back to the mid-1970s [8]. But, the theoretical understanding of the solid state reaction for its formation was investigated as early as in 1931 by Hedvall et al.

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[9] and in 1934 by Jander [10]. The effect of the following parameters; starting materials, optimum particle size, molar ratio, addition of mineralizers and kinetics of wollastonite formation, were tackled. Thus, raw materials; CaO, $Ca(OH)_2$, $CaCO_3$ and $CaSO_4$, limestone and silica as quartz sand slag arising from the phosphorous plants were used. The role of particle size in governing the reaction rate was determined by Kurczyk and Wührer [11] and by Kurczyk [12] that recommended reducing the particle size of quartz to a specific surface area 2 m^2/g i.e. about 0.1 μm. The former authors studied the effect of the $CaO:SiO_2$ ratio between 0.7 and 1.2, on the formation of wollastonite. They recommended a ratio of 0.9 for the best yield. Balkevich et al. [8] studied the effect of mineralizer namely a mixture of spodumen 1–3 wt% with fluorite 1–3% on the formation of wollastonite. Other mineralizers; alkali silicates, alkaline earth chlorides, fluorides or carbonates, wolframites and sulphates as well as glass frits were investigated.

An attempt to produce wollastonite from natural rocks and industrial silica wastes was carried out by Kotsis and Balogh [13]. They concluded that β-wollastonite (with little α-form) was achieved as the sole phase by heating at 1300 °C/1 h.

The present study aims at determining the optimum conditions for the production of wollastonite from industrial wastes and compare it with those obtained from chemical grade pure $CaCO_3$ and quartz or silica gel. The formation of wollastonite is followed by XRD and the microstructure observation by SEM.

2. Materials and methods

Wastes of marble processing produced by a local plant "El-Hassana Co." and silica fume product of the Egyptian Ferro-alloy Co. together with chemical grades calcium carbonate [HAS HMRZEL, The Netherlands], quartz [Fluka-Buchs] and silica gel [BDH, UK] powders were used to prepare wollastonite. The chemical analysis of the wastes was carried out by XRF and the mineral content by XRD using equipment type P Analytical, Axios XRF Spectrometer and Brukur Dg. Advance, respectively. The chemical composition of the wastes are shown in Table 1. The marble waste contains very minor amounts of impurities in the form of silica, alumina, alkali, iron and magnesium oxides. While the silica content in the fumes is about 91%. The surface area of the silica fumes is 21 m^2/g. The mean particle size for marble is <10 μm.

Table 1
Chemical constitution of wastes

Constituting oxides	Marble waste	Silica fumes
SiO_2	0.56	90.82
Al_2O_3	0.13	0.98
K_2O	0.72	1.28
Na_2O	–	0.80
MgO	1.22	0.60
CaO	53.5	0.50
Fe_2O_3	0.16	1.48
SrO	0.42	–
SO_3	0.11	0.60
Cl	0.31	–
LOI	41.5	1.97

The different sources were added to those of the carbonate in the stoichiometric composition i.e. $CaO:SiO_2$ is 1:1. Thermal behaviour of the waste and the stoichiometric composition was carried out by DTA and TG using equipment by Shimatzu type; DT50 and a heating rate of 5 °C/min.

Three compositions with the ratio 1:1 of $CaO:SiO_2$ fulfilled from both wastes [W], or $CaCO_3$ and silica gel [G] or $CaCO_3$ and pure quartz [Q]. The prepared powders were wet mixed in a ball mill for 1 h, then dried and pulverized. Cylinders 2.5 cm in diameter and 2 cm height were processed under uniaxial pressure of 20 MPa, dried and fired in an electric muffle furnace between 1000 and 1400 °C with a holding time of 1 h.

The crystalline phases developed on firing in the three series were followed by XRD equipment by Brukur Dg. Advance with Cu Kα radiation. The *d*-spacing which taken for the identification of the phases are shown in Table 2.

The microstructure of selected bodies was examined with a SEM Philips Model X130 equipped with EDAX to determine the ratio of the constituting elements.

3. Results and discussion

Thermal behaviour of the marble wastes in terms of DTA and TG, are displayed in Fig. 1a and b, respectively. A loss in weight equivalent to $\sim$42% indicates the relatively high content of $CaCO_3$ in the waste about 95%. DTA curve of the marble waste in Fig. 1a shows a sharp endothermic peak at $\sim$900 °C attributed to the dissociation reaction of $CaCO_3$. DTA curve of the stoichiometric from the wastes $CaO:SiO_2$, 1:1, Fig. 2, show a sharp endothermic peak at $\sim$900 °C attributed to the dissociation reaction of $CaCO_3$ and an exothermic at $\sim$950 °C attributed to the formation of metasilicate (calcium and magnesium silicate).

The XRD results of the three wollastonite groups (Figs. 3–5), reveal the following:

(1) The XRD of group (G) (Fig. 3), the attempt to synthesize wollastonite from silica gel and chemically pure grade $CaCO_3$, showed the formation of larnite which is dicalcium silicate instead of wollastonite and the crystallization of the silica gel giving cristobalite leaving lime unreacted. The content of lime decreases with increase of temperature, while the content of larnite and cristobalite increases. At

Table 2
Peak intensity and *d*-spacing of the identified phases

Phase	*h k l*	2θ (°)	*d* (A°)	Intensity (I/I_0)
Wollastonite	3 2 0	30.0	3.23	100
Pseudo-wollastonite	$2\,3\,\bar{1}$	27.5	2.97	100
Larnite	$\bar{1}\,0\,3$	41.2	2.18	70
Rankinite	0 3 1	33.0	2.71	100
Lime	2 0 0	37.5	2.41	100
Quartz	1 0 1	26.5	3.34	100
Cristobalite	1 0 1	21.9	4.05	100

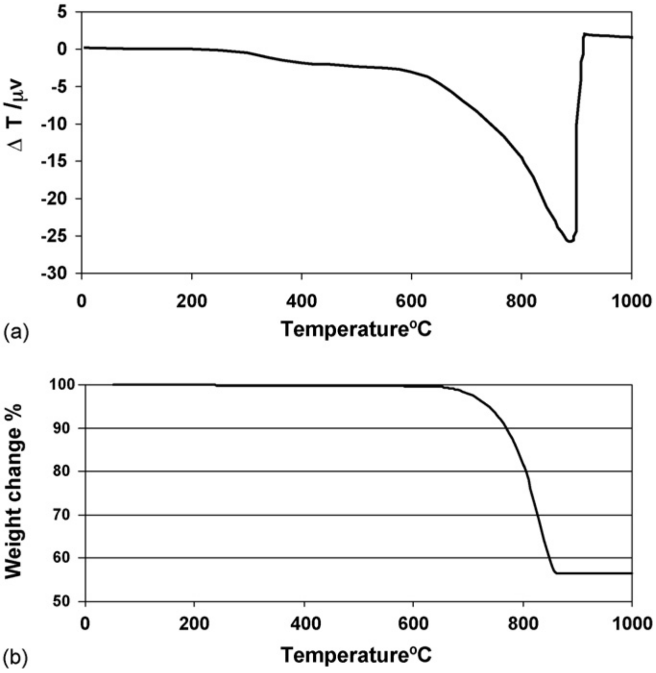


Fig. 1. Thermal behaviour of marble waste: (a) DTA and (b) TG.

1400 °C, the cristobalite decreases as it participated in the formation of glass.

(2) The XRD results of group (Q) (Fig. 4), the attempt to synthesize wollastonite from fine quartz and chemically pure grade CaCO$_3$, showed the formation of the same phases as group (G), namely; free lime, larnite and silica in the form of unreacted quartz. Wollastonite appeared in the specimens fired at 1100 °C, then disappeared at higher temperature entering in the formation of larnite. The content of quartz and lime [the starting material] decreased with rise of temperature. At 1400 °C, the different phases shared in the formation of a melt.

(3) The XRD results of group (W) (Fig. 5), the attempt to synthesize wollastonite from marble waste and silica fumes showed that the stoichiometric composition of lime and silica gave a mixture of larnite and wollastonite in the specimens fired at 1000, 1100, 1150 and 1200 °C. Moreover, the wollastonite phase changed to its polymorphic form pseudo-wollastonite together with formation of rankinite in the specimens fired at 1150 and 1200 °C. Therefore, excess silica was added to the stoichiometric composition to give the following molar ratios; 1:1.125, 1:1.166 and 1:1.25 and fired at 1150 °C. The results of XRD showed that the ratio 1:1.125 gave wollastonite as the sole phase. Cristobalite appeared in the two other ratios. Moreover, a mixture of two wollastonite polymorphs was recorded in composition CaO:SiO$_2$ (1:1.25) at 1250 °C.

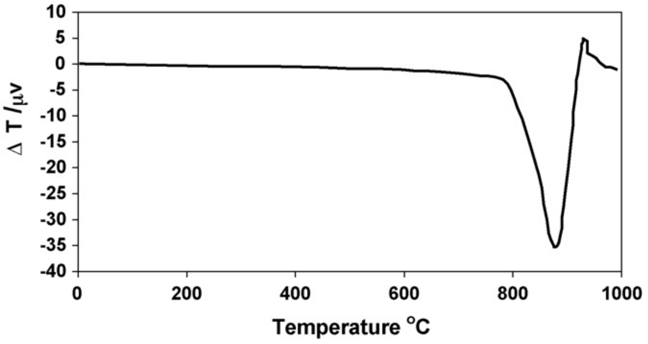


Fig. 2. DTA of stoichiometric composition 1:1 CaO:SiO$_2$ of group [W].

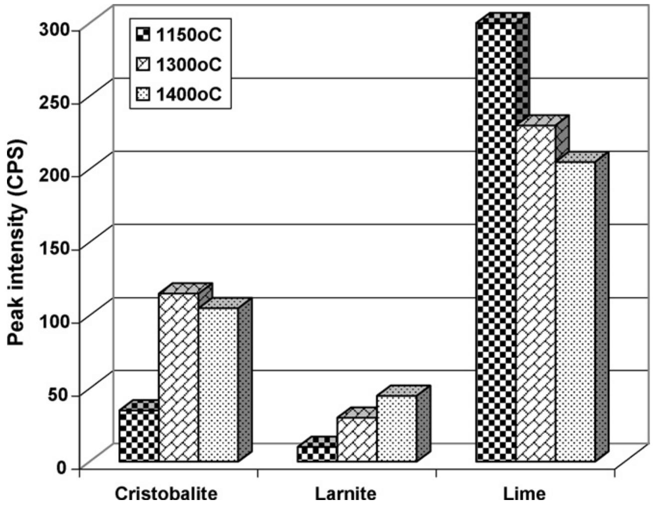


Fig. 3. Wollastonite formation from silica gel and pure CaCO$_3$, series [G].

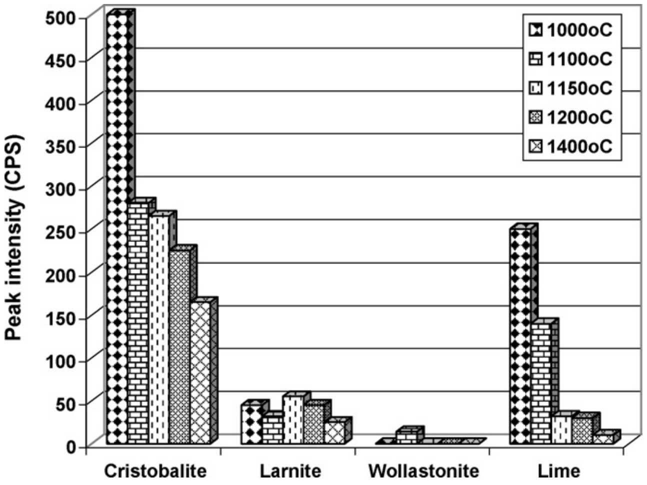


Fig. 4. Wollastonite formation from quartz and CaCO$_3$, group [Q].

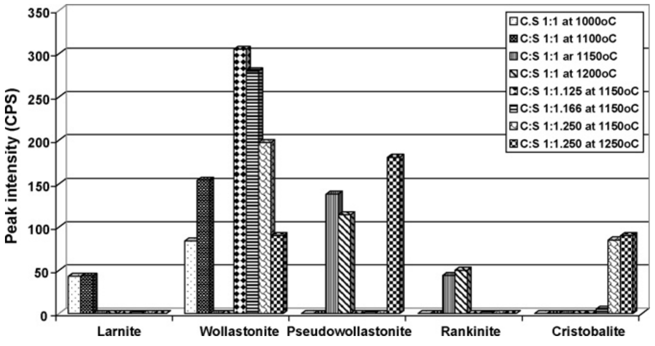
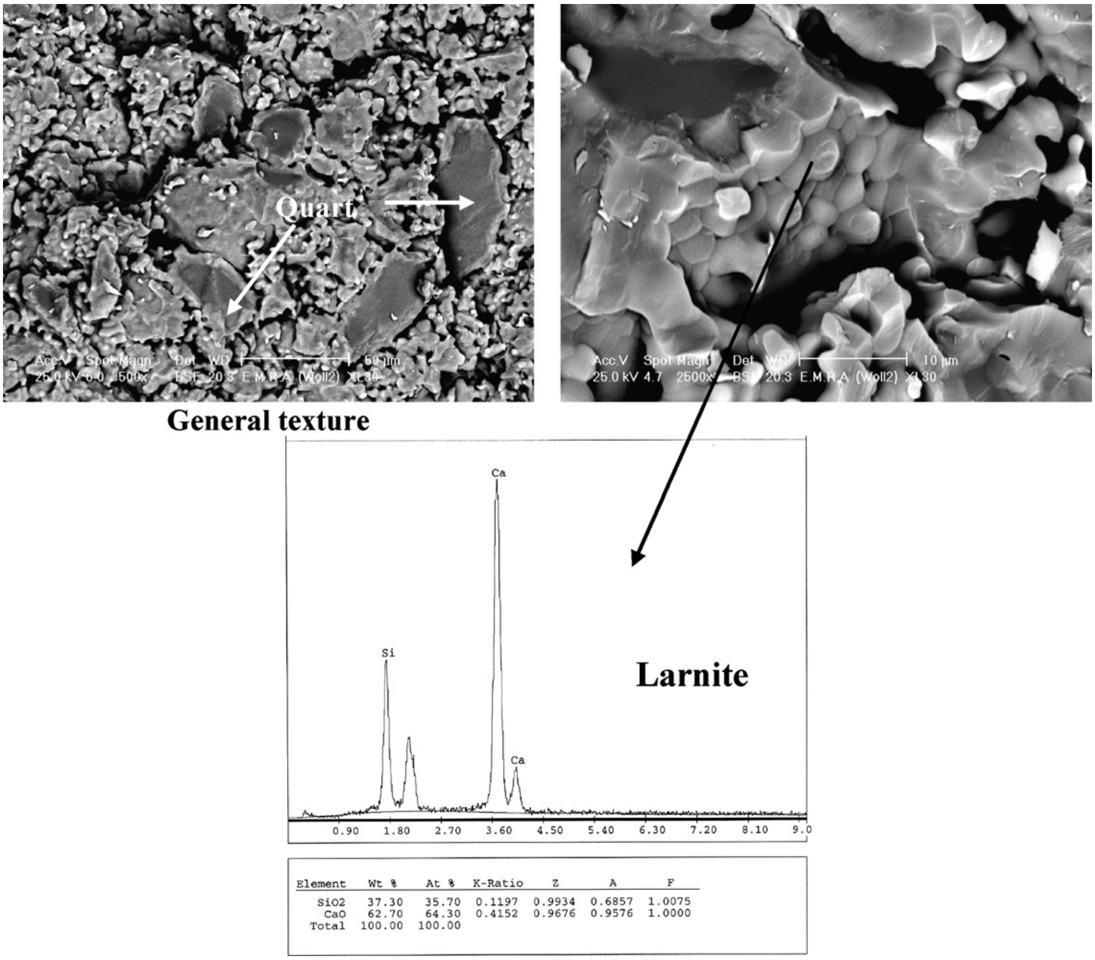


Fig. 5. Wollastonite from waste materials, group [W]. C:S is CaO:SiO$_2$.



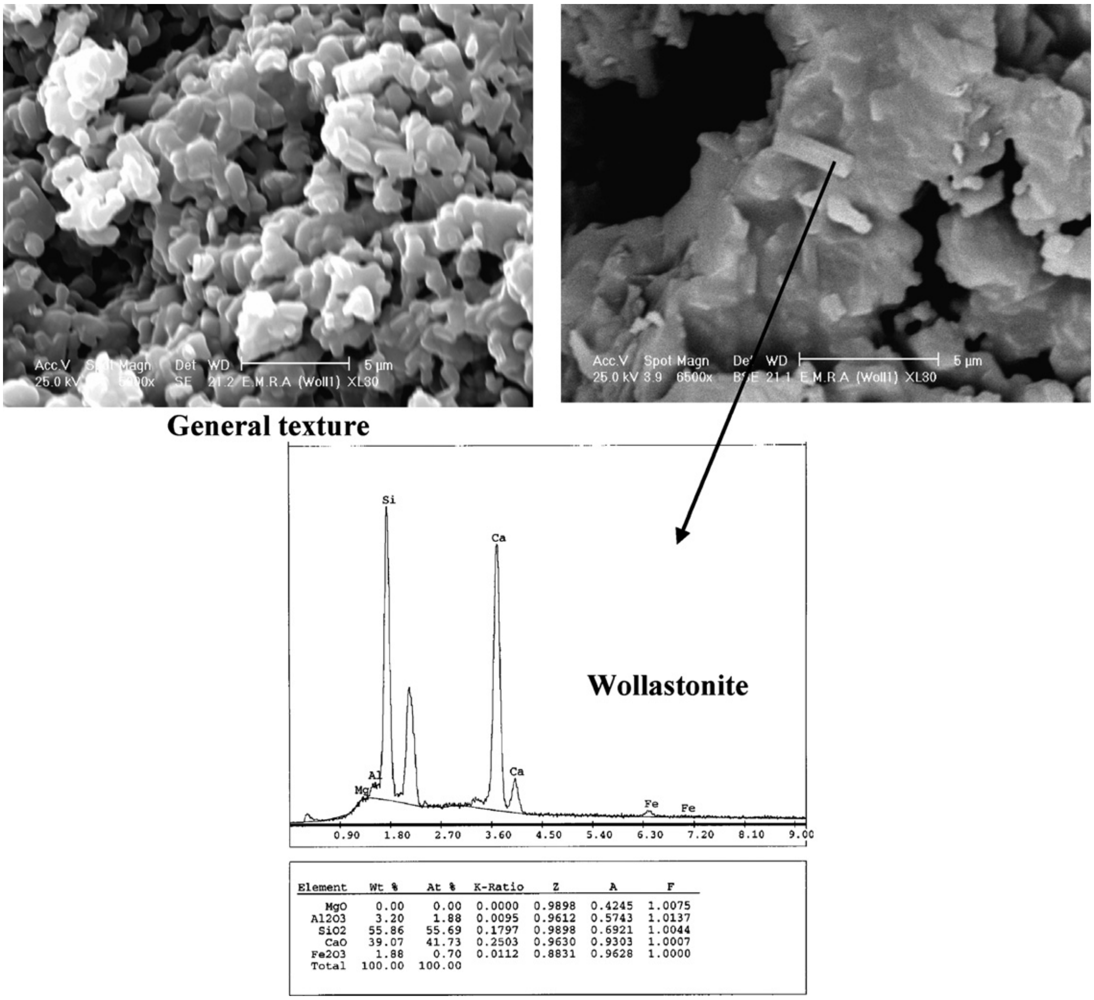
Element	Wt %	At %	K-Ratio	Z	A	F
SiO2	37.30	35.70	0.1197	0.9934	0.6857	1.0075
CaO	62.70	64.30	0.4152	0.9676	0.9576	1.0000
Total	100.00	100.00				

Fig. 6. SEM and EDAX of specimen of group [Q] fired at 1400 °C with ratio of CaO:SiO_2 1:1 showing sub-spherical grains of larnite.

SEM of group [Q] formed of $CaCO_3$ and quartz fired at 1400 °C/1 h, show the presence of unreacted quartz grains (dark grains) with the formation of larnite occurring as sub-spherical grains of uniform size about 2 μm in size, Fig. 6. The EDAX of such grains, showed that CaO and SiO_2 are the only components present. SEM of group [W] representing the wastes but with the ratio 1:1.125 fired at 1150 °C/1 h showed prismatic grains of wollastonite embedded in a melted matrix, Fig. 7. The EDAX of the prismatic grains shows the presence of Al_2O_3, Fe_2O_3, and MgO beside the main components CaO and SiO_2.

Wollastonite is formed in pure systems only in the presence of mineralizers or under hydrothermal conditions. The present results of group [G] and group [Q] using $CaCO_3$ and silica gel which is supposed to be highly active or quartz flour, failed to give wollastonite even on firing at high temperatures of 1400 °C. This is in accordance with the view of Balkevich et al. [8], who recorded the formation of wollastonite from siliceous limestone at 850 °C, where they attributed its formation to the intimate mixing and fineness of the components. Also, Kotsis and Balogh [13] reported the formation of wollastonite from limestone and silica gel at 1300 °C, but they did not mention that the presence of impurities in the limestone are responsible for its existence. As evident from the chemical composition of the limestone and silica fumes, they are impure.

Meanwhile, wollastonite was recorded in group [W] using the marble and silica fumes wastes. The presence of impurities in the form of alkali, iron, magnesia, aluminium oxides in both wastes, favoured the early formation of liquid phase at about 1100 °C which according to the phase diagram of CaO–SiO_2 should be at about 1450 °C [7]. The stoichiometric composition contains about 4.6% impurities, i.e. even higher than the amount recommended by the different authors for the formation of wollastonite 3.6% [13]. These impurities participated with the needed amount of silica in the formation of the melt reducing the stoichiometric ratio 1:1, for wollastonite formation as a sole phase, causing the crystallization of rankinite beside wollastonite in specimens fired at 1150 and 1200 °C. Therefore, increasing the proportion of silica was dictated to supply the needed amount for wollastonite formation. The ratio 1:1.125 was found to be the most appropriate as the two higher proportions 1:1.166 and 1:1.25 caused the appearance of cristobalite. According to Balkevich et al. [8], the reduction in the stoichiometric composition proceeded with formation of β-$2CaO{\cdot}SiO_2$, larnite yet in the present study $3CaO{\cdot}2SiO_2$ was formed. A certain excess of silica is needed to displace the reaction towards the wollastonite formation $CaO{\cdot}SiO_2$. In this case the silica reacts directly with the lime or with the larnite or rankinite formed to convert it into wollastonite.



Element	Wt %	At %	K-Ratio	Z	A	F
MgO	0.00	0.00	0.0000	0.9898	0.4245	1.0075
Al2O3	3.20	1.88	0.0095	0.9612	0.5743	1.0137
SiO2	55.86	55.69	0.1797	0.9898	0.6921	1.0044
CaO	39.07	41.73	0.2503	0.9630	0.9303	1.0007
Fe2O3	1.88	0.70	0.0112	0.8831	0.9628	1.0000
Total	100.00	100.00				

Fig. 7. SEM and EDAX of specimen of group [W] with ratio of CaO:SiO_2 1:1.125 fired at 1150 °C showing prismatic grains of wollastonite embedded in a melt.

4. Conclusion

- Pure systems failed to give wollastonite at all temperatures from 1000 up to 1400 °C. The presence of mineralizer is needed, this will be published later.
- The impurities in the form of alkalis, MgO and Fe_2O_3 in both of silica fume and marble wastes favoured the early formation of wollastonite at 1100 °C.
- The content of silica should be increased over the stoichiometric composition to get wollastonite as a sole phase, the most favourable molar ratio for the present wastes is 1:1.125.

References

[1] N.I. Demidenko, L.I. Podzorova, V.S. Rozanova, V.A. Skorokhoda, V.Ya. Shevchenko, Wollastonite as a new kind of natural material (a review), Steklo I keramika 58 (9) (2001) 15–17 (translated).

[2] L.M. Saltevskaya, Z.A. Livson, M.I. Ryshchenko, Wollastonite and its use in ceramic bodies, Steklo I keramika 31 (2) (1974) 22–24 (translated).

[3] G.M. Azorow, E.V. Maiorova, N.A. Oborina, A.V. Belyakov, Wollastonite raw materials and their applications (a review), Steklo I keramika 52 (9) (1995) 13–16 (translated).

[4] L.L. Hench, Bioceramic from concept to clinic, J. Am. Ceram. Soc. 74 (4) (1991) 1487–1510.

[5] L.H. Long, L.D. Chen, J. Chang, Low temperature fabrication and characterizations of β-$CaSiO_3$ ceramics, Ceram. Int. 33 (4) (2006) 457–460.

[6] H.R. Wenk, Polymorphism of wollastonite, Contr. Mineral Petrol. 22 (1969) 238–247.

[7] B. Philip, A. Muan, Phase diagram of CaO–SiO_2, J. Am. Ceram. Soc. (1959) 414.

[8] V.L. Balkevich, F.S. Peres, A.Y.U. Kogos, A.B. Kliger, M.A. Fishman, Synthesizing wollastonite from natural siliceous carbonate compositions, Steklo I keramika 42 (1) (1985) 20–21 (translated).

[9] J.A. Hedvall, E. Garping, N. Lindekrantz, L. Nelson, The role of ions and crystallographic transformation reactions in the solid state, Z. Anorg. Allg. Chem. 197 (1931) 399–421.

[10] W. Jander, The course of reactions in the solid state, Z. Anorg. Allg. Chem. 47 (1934) 235–238.

[11] H.G. Kurczyk, J. Wührer, Interceram. 20 (2) (1971) (cited in Ref. [13]).

[12] H.G. Kurczyk, Synthetic diopside and wollastonite—new raw materials for ceramic, Ceramurgia 8 (1978) 128–140.

[13] I. Kotsis, A. Balogh, Synthesis of wollastonite, Ceram. Int. 15 (1989) 79–85.